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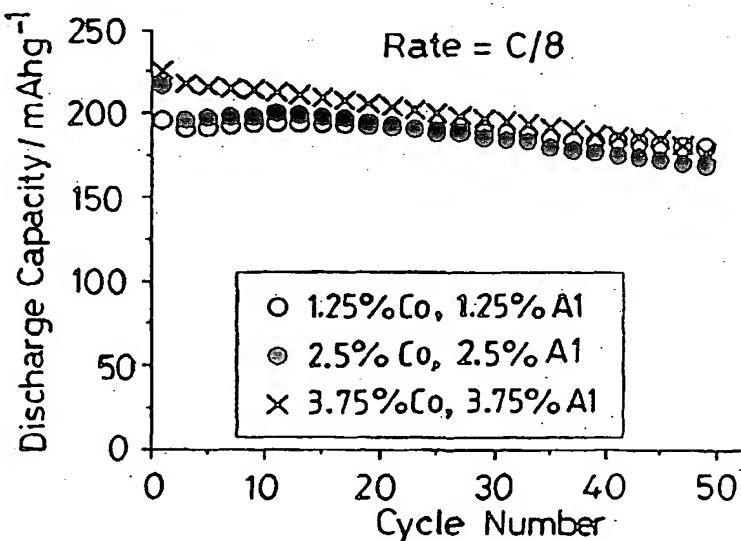
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[Continued on next page]

(54) Title: IMPROVEMENTS IN OR RELATING TO ELECTROCHEMICAL CELLS



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(57) Abstract: There is provided a manganese oxide material, wherein the material comprises a host material  $Q_yMn_xM_zO_x$ , where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure in which the ions are arranged in a series of generally planar layers, or sheets, stacked one on top of another. In a particularly preferred material Q is Li and M is either Co, Ni, Al, or Li. Particularly preferred combinations of M and a dopant are Ni,Co; Al,Co; Li,Cu; Li,Al; and Li,Zn. A method of preparing the material is also disclosed.



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Title: Improvements in or Relating to Electrochemical Cells

Field of Invention

This invention concerns electrochemical cells and relates to material with a layered structure for use in such cells, a method for producing the layered materials, and a cell having the layered materials as the positive electrode.

Background to the Invention

Electrochemical cells generally have a negative electrode, a positive electrode, and an electrolyte placed between the electrodes. The electrolyte is chosen so that transfer of ions between the two electrodes occurs, thus producing an electrical current. One example of an electrochemical cell is a rechargeable battery. The use of layered materials such as lithium cobalt oxide,  $\text{LiCoO}_2$ , as the positive electrode in such a rechargeable battery is well established. The layered material consists of sheets of oxygen ions stacked one on top of the other. Between the first and second layers of oxygen are located the cobalt ions, with the lithium ions being located between the second and third oxygen layers. Use of  $\text{LiCoO}_2$  in rechargeable batteries allows greater energy storage per unit weight and volume than is possible in conventional rechargeable batteries such as nickel-cadmium. However  $\text{LiCoO}_2$  has disadvantages in that it is somewhat toxic, is less safe than is desirable, has limited energy storage capacity, and the cobalt containing materials from which it is produced are expensive and scarce.

Attempts have been made to use other compounds with a similar layered structure to that of,  $\text{LiCoO}_2$ , such as  $\text{LiNiO}_2$ , and  $\text{LiFeO}_2$ . EP 0 017 400 discloses a range of compounds having layers of the  $\alpha\text{-NaCrO}_2$  structure. In an International Patent Application, Publication No. WO97/26683, we disclosed the synthesis and viability of materials of the form  $\text{Q}_q\text{Mn}_y\text{M}_z\text{O}_2$ , where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and the material is a layered structure.

It is one aim of the present invention to provide a further layered manganese oxide material which can be used in electrochemical cells.

### Summary of the Invention

According to one aspect of the present invention, there is provided a manganese oxide material, wherein the material comprises a host material  $Q_qMn_yM_zO_x$ , where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure. Any number of dopants may be substituted into the host material, with the number of simultaneously occurring dopants possible only being restricted by the requirement to retain a layered structure. Such a material may be written as  $Q_qMn_yM_zA_aB_bC_c\dots\gamma_nO_x$ , where A, B, C....  $\gamma_n$  are dopants. Typically for such a material the values of z, a, b, c,...,n will be chosen to sum equal to one.

A layered structure is one in which the ions are arranged in a series of generally planar layers, or sheets, stacked one on top of another. In general, each layer contains ions of one particular element. Thus, when z is equal to zero and q is greater than zero, the layering will consist of sheets of oxide ions which are separated by alternating layers of Q ions and Mn ions, i.e. the layers order as a layer of oxide ions, a layer of Mn ions, a layer of oxide ions, a layer of Q ions and a layer of oxide ions; this is repeated throughout the structure.

Q is preferably chosen from Group I elements, i.e. K, Li, Rb, and in a particularly preferred material is Li so that the host material is of the form  $Li_wMn_yM_zO_x$ , where w is any number greater than zero.

Where z is not equal to zero, the M ions will occupy sites in the Mn layers, and if desired M within the host material can be viewed as a first dopant with at least one further dopant being substituted within the material.

Where z is not equal to zero, the element M is typically chosen from Group II elements, the transition elements or from Group III elements. Suitable elements include Be, Mg, Ca, Sc,

Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Al, Ga, P. However Group I elements such as Li may also be used as a dopant.

In a particularly preferred material according to the invention, Q is Li and M is either Co, Ni, Al, or Li.

Preferably at least one dopant is chosen from Group II elements, the transition elements or from Group III elements. Suitable elements include Ni, Al, Co, Mg, Zn and Cu.

Particularly preferred combinations of M and a dopant are Ni, Co; Al, Co; Li, Co; Li, Ni; Li, Mg; Li,Cu; Li,Al; and Li, Zn.

According to a further aspect of the invention, there is provided a method of preparing a manganese oxide material of the invention, comprising processing an intermediate material  $X_xMn_yM_zA_aB_bO_x$  (or any number of elements n additional to M, A and B), where X is a Group I element not being lithium, M, A and B are any element, a, x and y are each any number greater than zero, and z, and b are any number greater than or equal to zero, by an ion exchange reaction with a reactant containing lithium ions, so as to replace X with lithium and produce a material of the form  $Li_wMn_yM_zA_aB_bO_x$ , where w is any number greater than zero, and the material has a layered structure. If M is to be incorporated, then z is chosen to be greater than zero.

Preferably X is chosen to be Na, so that the intermediate material is of the form  $Na_xMn_yM_zA_aB_bO_x$ .

The reactant may be any suitable lithium salt, such as LiBr or LiCl. Preferably the ion exchange reaction is achieved by heating the reactant and intermediate material under reflux. Typically n-pentanol, n-hexanol, ethanol or n-octanol are used as the reflux agent, with the reflux period being 96 hours.

In a particularly preferred exchange reaction, the ion exchange occurs at room temperature and in water.

According to a further aspect of the invention, there is provided a method of preparing a manganese oxide material of the invention, comprising processing a precursor material  $Q_qMn_yM_zA_aB_bO_x$ , where Q and M are each any element, q and y are each any number greater than zero, z and b are any number greater than or equal to zero, and a is greater than zero by carrying out an ion removal reaction, so as to remove Q and produce a material of the form  $Mn_yM_zA_aB_bO$ , with a layered structure.

Ion removal is conveniently achieved by electrochemical extraction, using the precursor material as the working electrode in an electrochemical cell. This is of particular advantage in preparation of materials of the form  $Mn_yM_zA_aB_bO_x$ . For preparation of these materials, Q is preferably chosen from the Group I or Group II elements, such as Na, K, Rb, Mg or Ca. The  $Mn_yM_zA_aB_bO_x$  may be subsequently processed to insert lithium so as to produce  $Li_wMn_yM_zA_aB_bO_x$ .

According to another aspect of the invention, there is provided an electrochemical cell, wherein the positive electrode is of the form  $Li_qMn_yM_zA_aB_bO_x$  where M, A and B are any elements, x, y, z and a are any number greater than zero, and q and b are each any number greater than or equal to zero. The use of the manganese in the electrode avoids the need for use of cobalt or nickel which is of advantage as manganese is less toxic, safer, more abundant and cheaper than cobalt and nickel.

A rechargeable battery is an example of an electrochemical cell with which the invention may be used.

The invention will now be described by way of example, and with reference to the accompanying Figures in which:

Figures 1(a) and 1(b) show the observed diffraction data of a material according to the invention, where M is Li and the dopant is Co, Figure 1(a) being an X-ray diffraction trace and Figure 1(b) a neutron diffraction trace;

Figure 2 shows the discharge capacity of a cell incorporating a further material according to the invention on successive discharge cycles, where M is Ni and the dopant Co;

Figure 3 shows the discharge capacity of a cell incorporating a further material according to the invention on successive discharge cycles, where M is Co and the dopant Al; and

Figure 4 shows the discharge capacity of a cell incorporating a further material according to the invention on successive discharge cycles, where M is Li and the dopant is either Cu or Al or Zn.

### Description

The preparation of materials of the form  $Q_qMn_yM_zO_2$  incorporating one or more dopants, and the experimental verification of the structure of such materials and their properties as an electrode for an electrochemical cell will be described. If desired, one can view  $Q_qMn_yO_2$  as the base or host material into which M and/or at least one other dopant are substituted, producing a double dopant system. However substitution is only limited by the requirement to have a layered structure, and multiple dopants can be substituted into the original structure.

### **Preparation**

Preparation of the materials requires two stages:

- 1) The preparation of the intermediate material, sodium manganese oxide,  $NaMnO_2$  combined with the dopants, i.e. of the form  $Na_qMn_yM_zA_aB_bO_x$ , where A is one additional dopant, and B is another additional dopant; and
- 2) Ion exchange reaction.

#### **Stage 1**

##### **(a) Solid State Preparation**

Appropriate quantities of the Na source such as  $Na_2CO_3$ , a Manganese oxide such as  $Mn_2O_3$ ,  $MnO$  or  $MnO_2$  and oxides of the dopant elements are weighed out and intimately ground together with or without a dispersant such as acetone. As will be apparent to a person skilled in the art,  $NaOH$ ,  $Na(CH_3CO_2)$  or any other solid Na compound which decomposes on heating to yield the oxide can be used instead of  $Na_2CO_3$ , and any solid Mn source which decomposes on heating to yield the oxide can be used to provide a source of Mn. Any

source of the elements M, A, B etc. which decomposes on heating to yield the oxide can be used to supply the dopants.

The resulting homogenous mixture of Na source, Mn source and dopant sources is heated in a furnace until a material of the form  $\text{Na}_q\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$  is produced. Whether an air, reducing or oxidising atmosphere is required within the furnace depends on the elements M, A, B and the furnace heating and cooling characteristics chosen will depend on M, A and B. Typically temperatures of between 250°C and 1500°C are chosen for anything between 1-96 hours and the samples may be furnace cooled or cooled more quickly.

The intermediate material can also be prepared from solution, and where required solution preparation is as follows.

#### (b) Solution Preparation

Suitable salts of Na, Mn, M, A, B etc. which are soluble in  $\text{H}_2\text{O}$ , ethanol, n-hexanol or similar solvents, for example  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCH}_3\text{CO}_2$ ,  $\text{Mn}(\text{CH}_3\text{CO}_2)_2$  and  $\text{A}(\text{CH}_3\text{CO}_2)_n$ ,  $\text{B}(\text{CH}_3\text{CO}_2)_n$  are weighed out and added to the solvent. After mixing, the solvent is removed by heating and if required using reduced pressure. The resulting homogenous mixture is then heated at a low temperature between 80-150°C for between 1-5 hours, and then at temperatures between 250-1500°C for 1-96 hours in air, or if appropriate depending on the combination of elements M, A, B in a more reducing or more oxidising atmosphere. As before the samples may be furnace cooled or cooled more quickly, such as by air cooling.

#### Stage 2

An excess, typically 8-15 fold of a Lithium salt such  $\text{LiBr}$ ,  $\text{LiCl}$  or  $\text{LiNO}_3$ , is added to a solvent such as ethanol, butanol, n-hexanol, n-octanol, acetonitrile, water or a combination of some of these. To this mixture is added the intermediate material prepared either by solid state reaction or from solution as above, and the various constituents allowed to react for between 6 and 96 hours at a suitable temperature. Where the reaction is carried out at elevated temperatures, then a condenser is fitted permitting reflux. For example ion exchange in ethanol may be carried out by refluxing at 80°C or in the case of n-hexanol 160°C. Particularly of interest is that the ion exchange reaction is possible at room

temperature and in water. After reaction the mixture is subjected to filtration under suction and then washed with a solvent used for exchange, typically alcohol or alcohol and water, before being dried.

Alternatively ion exchange is carried out in a molten salt containing a Lithium source. For this, the sample is mixed with the ion exchange medium and heated until the medium is molten. The temperature is maintained for 1-96 hours until exchange is complete. After cooling the ion exchange medium is removed by washing in H<sub>2</sub>O, alcohol or other solvent. The resulting material is dried by heating under vacuum.

The structure of the resultant product was then examined by X-ray diffraction or by neutron diffraction. Determination of the structure by neutron diffraction requires the observed diffraction data from a representative sample of the product to be compared to theoretical diffraction data for a variety of structural models. The correct structural model produces the best fit between theoretical and observed data. Typically trial models are selected by looking at the structures of similar families of compounds, or from the structures of the compounds that formed the product.

Time-of-flight powder neutron diffraction data were collected on the POLARIS high intensity, medium resolution diffractometer at the ISIS pulsed source at the Rutherford Appleton Laboratory. Data from the highest resolution backscattering bank of detectors were used for structural analysis.

Figure 1(a) shows the X-ray diffraction pattern of Li<sub>x</sub>Mn<sub>0.95</sub>Li<sub>0.025</sub>Co<sub>0.025</sub>O<sub>2</sub>, with thus M being Li and the additional dopant being Co and Figure 1(b) shows the neutron diffraction pattern of the same compound. Various other combinations of dopants have been investigated including the following (where the first element is equivalent to M in the general formula given above and the second element the additional dopant): Co, Ni; Co, Al; Li, Co; Li, Ni; Li, Al; Li, Mg; Li, Zn; Li, Cu.

The materials produced in accordance with the present invention have a layered structure in which the Mn, Li and O ions are arranged separately in a series of generally planar layers, or

sheets, stacked one on top of another, with the dopants substituting into these layers. Generally the dopants substitute randomly into the Mn layers, although some of the dopant ions may be present in the Li layers. The layering will thus consist of sheets of oxide ions which are separated by alternating layers of Li ions and Mn ions, i.e. the layers order as a layer of oxide ions, a layer of Mn ions, a layer of oxide ions, a layer of Q ions and a layer of oxide ions; this is repeated throughout the structure.

The layered structure possesses a crystal symmetry lower than rhombohedral and is generally monoclinic. The monoclinic structure possesses one 2-fold axis and/or one plane of symmetry, its unit cell possessing three unequal axes, one axis being perpendicular to the other two axes which are inclined at an oblique angle. In such a structure the Mn ions are not equally spaced from all nearest neighbour oxide ions, i.e. the three oxide ions in the adjacent upper layer and the three oxide ions in the adjacent lower layer, but rather are distorted from equal spacing so that the Mn-O bond distance varies. An equivalent view of this is that the layered structure comprises layers of MnO<sub>6</sub> polyhedra separated by layers of other ions, for example lithium ions.

Lattice parameter data for selected materials are given below:

Nominal y	a/ Angstrom	c/Angstrom	c/a
0.025	2.8652 (4)	14.674 (2)	5.121
0.05	2.8731 (3)	14.638 (1)	5.095
0.10	2.8667 (3)	14.612 (2)	5.097
0.20	2.8699 (3)	14.620 (1)	5.094

Table 1: Lattice parameter data for Li<sub>x</sub>Mn<sub>1-y</sub>Ni<sub>y/2</sub>Co<sub>y/2</sub>O<sub>2</sub> system

Nominal y	a/ Angstrom	c/Angstrom	c/a
0.05	2.8672 (3)	14.618 (1)	5.098

Table 2: Lattice parameter data for Li<sub>x</sub>Mn<sub>1-y</sub>Li<sub>y/2</sub>Ni<sub>y/2</sub>O<sub>2</sub> system

Nominal y	a/ Angstrom	C/Angstrom	c/a
0.05	2.8614 (3)	14.614 (1)	5.107

Table 3: Lattice parameter data for  $\text{Li}_x\text{Mn}_{1-y}\text{Li}_{y/2}\text{Co}_{y/2}\text{O}_2$  system

Nominal y	a/ Angstrom	C/Angstrom	c/a
0.05	2.8690 (4)	14.641 (2)	5.103

Table 4: Lattice parameter data for  $\text{Li}_x\text{Mn}_{1-y}\text{Li}_{y/2}\text{Mg}_{y/2}\text{O}_2$  system

The performance of various materials in accordance with the present invention in an electrochemical cell is shown in Figures 2 to 4. These Figures show the discharge capacity of the material used in an electrolytic cell during successive discharge cycles. The cell was cycled at 30° C at a constant current C of 0.5mAcm<sup>-2</sup> between the potential limit 2.4 and 4.6 V to simulate the behaviour of a rechargeable battery. These Figures demonstrate that lithium can be chemically or electrochemically extracted from and reinserted into these materials, i.e. it is an intercalation/insertion electrode.

Figure 2 shows the discharge capacity in mAhg<sup>-1</sup> over 150 cycles at C/8 and 1C for  $\text{Li}_x\text{Mn}_{0.95}\text{Ni}_{0.025}\text{Co}_{0.025}\text{O}_2$ , i.e. where M is Ni and the additional dopant is Co.

Figure 3 shows the discharge capacity in mAhg<sup>-1</sup> over 50 cycles at C/8 for  $\text{Li}_x\text{Mn}_{1-y}\text{Co}_{y/2}\text{Al}_{y/2}\text{O}_2$ , i.e. where M is Co and the additional dopant is Al, for varying percentages of Co and Al. The discharge capacity is similar for all three compositions shown and is similar to the discharge at C/8 for  $\text{Li}_x\text{Mn}_{0.95}\text{Ni}_{0.025}\text{Co}_{0.025}\text{O}_2$ .

Figure 4 shows the discharge capacity in mAhg<sup>-1</sup> over 150 cycles at a rate of C/4/ 50mA<sup>-1</sup> between voltage limits of 2.4-4.6V for  $\text{Li}_x\text{Mn}_{0.95}\text{M}_{0.025}\text{A}_{0.025}\text{O}_2$ , i.e. where M is Li and the additional dopant A is Cu, or Al or Zn. Better discharge properties are seen for the materials having the dopant pairs Li, Cu and Li Al.

Claims

1. A manganese oxide material, wherein the material comprises a host material  $Q_qMn_yM_zO_x$ , where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure.
2. A manganese oxide material according to claim 1, wherein Q is chosen from Group I elements.
3. A manganese oxide material according to claim 2, wherein Q is Li and the host material is of the form  $Li_wMn_yM_zO_x$ , where w is any number greater than zero.
4. A manganese oxide material according to any of the preceding claims, wherein the element M is chosen from Group I, Group II elements, the transition elements or from Group III elements.
5. A manganese oxide material according to any of the preceding claims, wherein Q is Li and M is either Co, Ni, Al, or Li.
6. A manganese oxide material according to any of the preceding claims, wherein at least one dopant is chosen from Group II elements, the transition elements or from Group III elements.
7. A method of preparing a manganese oxide material comprising processing an intermediate material  $X_xMn_yM_zA_aB_bO_x$  (or any number of elements n additional to M, A and B), where X is a Group I element not being lithium, M, A and B are any element, a, x and y are each any number greater than zero, and z and b are any number greater than or equal to zero, by an ion exchange reaction with a reactant containing lithium ions, so as to replace X with lithium and produce a material of the form  $Li_wMn_yM_zA_aB_bO_x$ , where w is any number greater than zero, and the material has a layered structure.

8. A method according to claim 7, wherein X is Na, so that the intermediate material is of the form  $\text{Na}_x\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$ .
9. A method according to claim 7 or claim 8, wherein the ion exchange reaction is achieved by heating the reactant and intermediate material under reflux.
10. A method according to claim 9, wherein the ion exchange reaction occurs at room temperature and in water.
11. A method of preparing a manganese oxide material comprising processing a precursor material  $\text{Q}_q\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$ , where Q and M are each any element, q and y are each any number greater than zero, z and b are any number greater than or equal to zero, and a is greater than zero by carrying out an ion removal reaction, so as to remove Q and produce a material of the form  $\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}$ , with a layered structure.
12. A method according to claim 11, wherein ion removal is conveniently achieved by electrochemical extraction, using the precursor material as the working electrode in an electrochemical cell.
13. An electrochemical cell, wherein the positive electrode is of the form  $\text{Li}_q\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$  where M, A and B are any elements, x, y, z and a are any number greater than zero, and q and b are each any number greater than or equal to zero.
14. A rechargeable battery comprising an electrochemical cell according to claim 13.

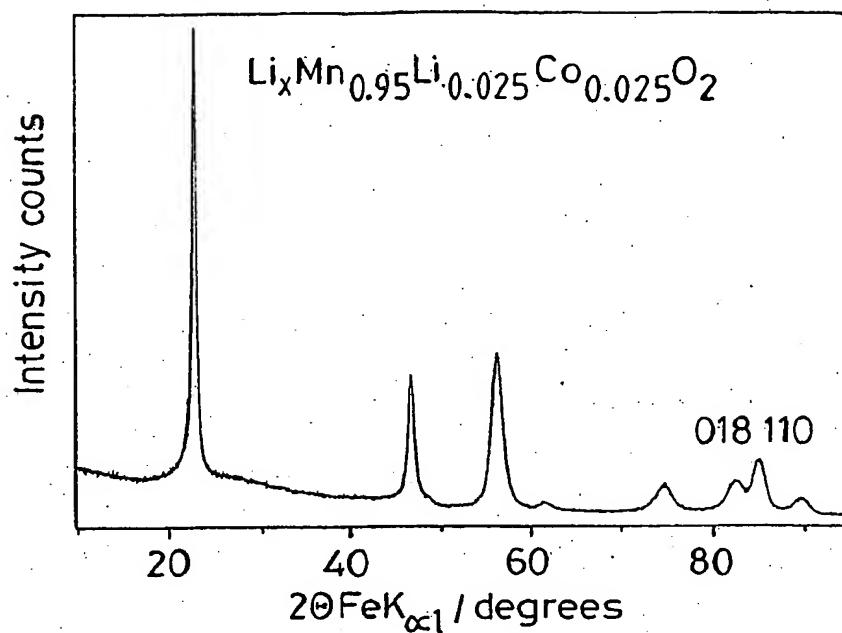


Fig. 1(a)

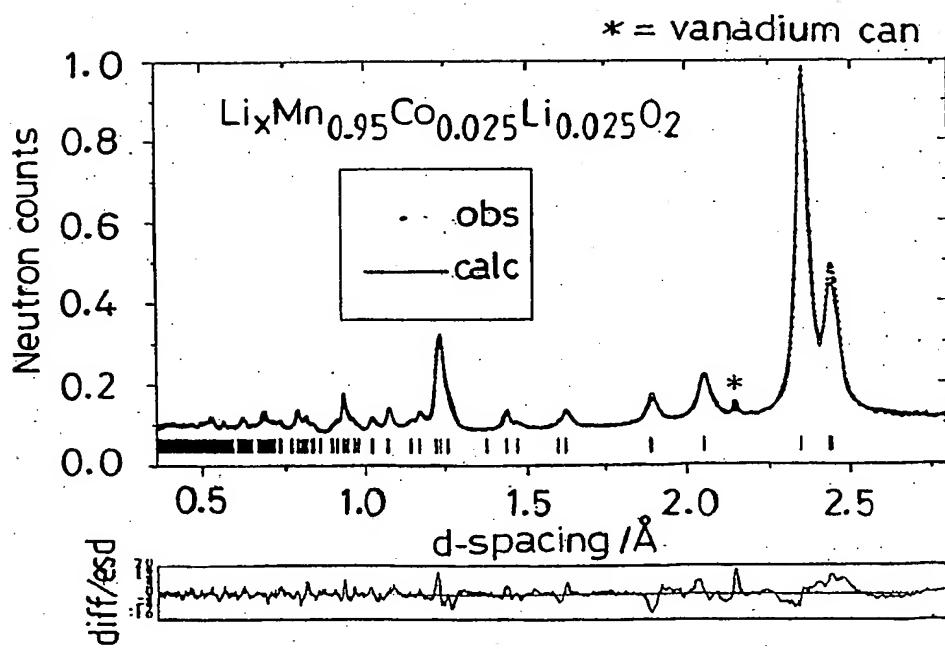


Fig. 1(b)

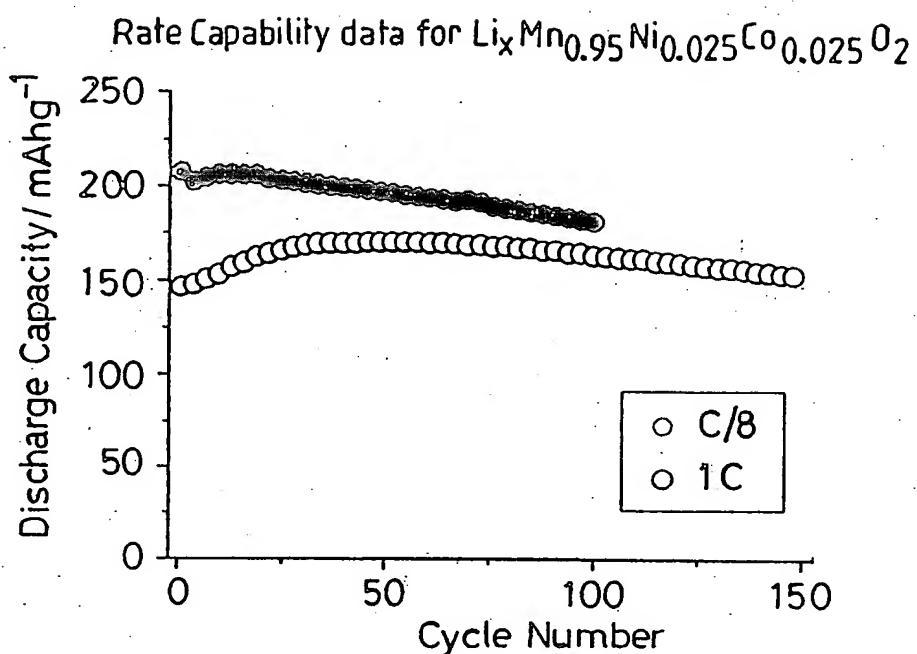


Fig. 2

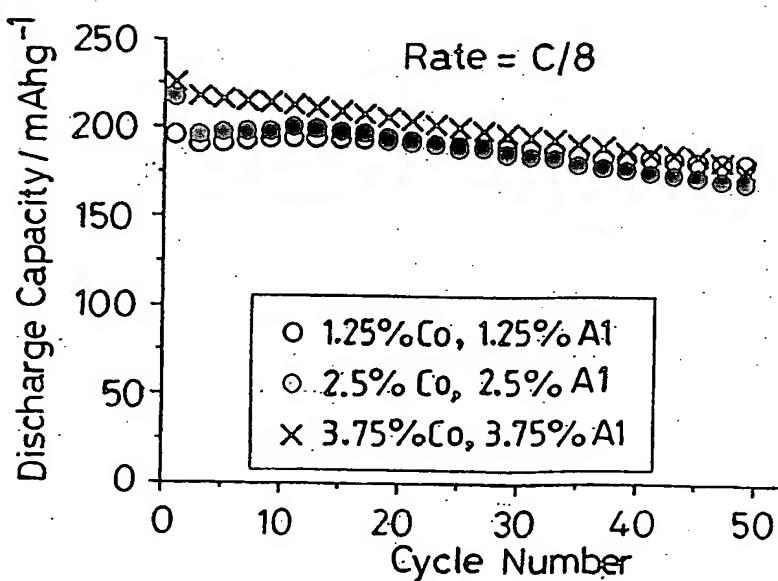


Fig. 3

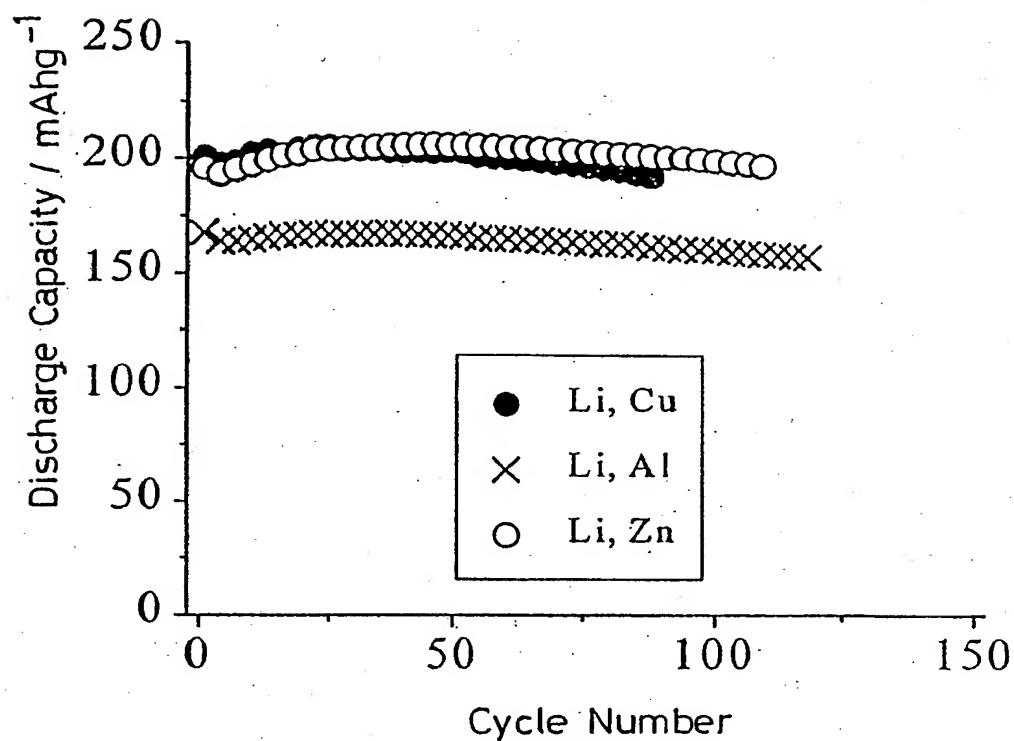


Fig. 4

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(54) Title: MANAGANESE OXIDE MATERIAL FOR ELECTROCHEMICAL CELLS

(57) Abstract: There is provided a manganese oxide material, wherein the material comprises a host material  $Q_{\ell}q?Mn_{\ell}y?M_i z?O_i x?$ , where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure in which the ions are arranged in a series of generally planar layers, or sheets, stacked one on top of another. In a particularly preferred material Q is Li and M is either Co, Ni, Al, or Li. Particularly preferred combinations of M and a dopant are Ni,Co; Al,Co; Li,Cu; Li,Al; and Li,Zn. A method of preparing the material is also disclosed.

# INTERNATIONAL SEARCH REPORT

International Application No

PC 7aB 02/02905

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 H01M4/50 C01G45/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, PAJ, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 1 180 810 A (NISSAN MOTOR) 20 February 2002 (2002-02-20) examples 1-21 ----- PATENT ABSTRACTS OF JAPAN vol. 2002, no. 06, 4 June 2002 (2002-06-04) & JP 2002 050401 A (NISSAN MOTOR CO LTD), 15 February 2002 (2002-02-15) page 9 ----- US 2002/012830 A1 (MUNAKATA FUMIO ET AL) 31 January 2002 (2002-01-31) figure 3 ----- -/-	1-6,13, 14
P,X		1-6,13, 14
P,X		1-6,13, 14

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 May 2004

Date of mailing of the international search report

12.0.09.04

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/02905

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 03, 3 April 2002 (2002-04-03) & JP 2001 328818 A (NATIONAL INSTITUTE FOR MATERIALS SCIENCE; TODA KOGYO CORP; JAPAN STORAG), 27 November 2001 (2001-11-27) abstract ----- EP 1 130 665 A (NISSAN MOTOR) 5 September 2001 (2001-09-05) examples 1-16 -----	1-9,13, 14
P,X	PATENT ABSTRACTS OF JAPAN. vol. 2000, no. 23, 10 February 2001 (2001-02-10) & JP 2001 167763 A (HITACHI LTD; HITACHI MAXELL LTD), 22 June 2001 (2001-06-22) page 5; table 1 -----	1-6,13, 14
X	ROBERTSON ET AL.: CHEM. MATER, vol. 13, no. 7, 22 June 2001 (2001-06-22), pages 2380-2386, XP002282136 the whole document -----	1-9,13, 14
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 22, 9 March 2001 (2001-03-09) & JP 2001 143710 A (SAMSUNG SDI CO LTD), 25 May 2001 (2001-05-25) abstract -& US 6 274 273 B1 14 August 2001 (2001-08-14) example 1 -----	1-6,13, 14
X	WO 01/15252 A (SUEYOSHI TSUYOSHI ; MIYAGI HIDEKAZU (JP); MITSUBISHI CHEM CORP (JP)) 1 March 2001 (2001-03-01) page 28; table 2 -----	1-6,13, 14
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 16, 8 May 2001 (2001-05-08) & JP 2001 023640 A (SEIMI CHEM CO LTD), 26 January 2001 (2001-01-26) abstract -----	1-6,13, 14
X	WO 01/01505 A (MINAGAWA YUKINORI ; OKAHARA KENJI (JP); SHIZUKA KENJI (JP); AOSHIMA) 4 January 2001 (2001-01-04) abstract -----	1-6,13, 14
X	US 6 168 887 B1 (DAHN JEFFREY R ET AL) 2 January 2001 (2001-01-02) examples 1-4 -----	1-9,13, 14
		-/-

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/02905

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document; with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 13, 5 February 2001 (2001-02-05) & JP 2000 294242 A (SEIMI CHEM CO LTD), 20 October 2000 (2000-10-20) abstract	1-6,13, 14
X	PAULSEN ET AL.: J. ELECTROCHEMICAL SOCIETY, vol. 147, no. 8, 2000, pages 2862-2867, XP001181450 the whole document	1-10,13, 14
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 03, 30 March 2000 (2000-03-30) & JP 11 339771 A (FUJI PHOTO FILM CO LTD), 10 December 1999 (1999-12-10) abstract	1-6,13, 14
X	PAULSEN ET AL.: J. ELECTROCHEM. SOC., vol. 146, no. 10, 1999, pages 3560-3565, XP002282137 the whole document	1-9,13, 14
X	ARMSTRONG ET AL.: J. SOLID STATE CHEM., vol. 145, 1999, pages 549-556, XP002282138 the whole document	1-9,13, 14
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 067209 A (SANYO ELECTRIC CO LTD), 9 March 1999 (1999-03-09) abstract	1-6,13, 14
X	WO 99/05734 A (KUBO KOICHI ; TAKEUCHI HAJIME (JP); TOKYO SHIBAURA ELECTRIC CO (JP)) 4 February 1999 (1999-02-04) -& US 6 458 487 B1 1 October 2002 (2002-10-01) tables 1-4	1-6,13, 14
X	ARMSTRONG ET AL.: J. MATER., vol. 9, no. 1, 1999, pages 193-198, XP002282139 page 197	1-9,13, 14

-/-

## INTERNATIONAL SEARCH REPORT

Intelli Application No  
PC17AB 02/02905

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 02, 28 February 1997 (1997-02-28) & JP 08 273665 A (MITSUI MINING & SMELTING CO LTD), 18 October 1996 (1996-10-18) abstract ----- -----	1-6,13, 14
X	US 6 214 493 B1 (ARMSTRONG ANTHONY ROBERT ET AL) 10 April 2001 (2001-04-10) the whole document -----	1-14

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 02/02905

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-14 (partially)

#### Remark on Protest

- The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: -

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently, the search has been restricted to lithium manganese oxide having a dopant M and an additional dopant A i.e. compounds having the following composition LiMn<sub>x</sub>Al<sub>y</sub>Ni<sub>z</sub>Mg<sub>w</sub>O where M is Li, Co, Al, Ni and A is Co, Cu, Al, Ni and Mg.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-14 (partially)

Claims 1-6 relate to a lithium manganese oxide of the following composition  $\text{LiMnMAO}$  wherein M is Li and the additional dopant A is Co.

Claims 7-12 relate to a method of preparation of an oxide according to claim 1-6.

Claims 13, 14 relate to the use of the oxide of claim 1-6 in a electrochemical cell and the use of such a cell in arechargeable battery.

2. claims: 1-14 (partially)

Claims 1-6 relate to a lithium manganese oxide of the following composition  $\text{LiMnMAO}$  wherein M is Li and the additional dopant A is Mg.

Claims 7-12 relate to a method of preparation of an oxide according to claim 1-6.

Claims 13, 14 relate to the use of the oxide of claim 1-6 in a electrochemical cell and the use of such a cell in arechargeable battery.

3. claims: 1-14 (partially)

Claims 1-6 relate to a lithium manganese oxide of the following composition  $\text{LiMnMAO}$  wherein M is Li and the additional dopant A is Cu.

Claims 7-12 relate to a method of preparation of an oxide according to claim 1-6.

Claims 13, 14 relate to the use of the oxide of claim 1-6 in a electrochemical cell and the use of such a cell in arechargeable battery.

4. claims: 1-14 (partially)

Claims 1-6 relate to a lithium manganese oxide of the following composition  $\text{LiMnMAO}$  wherein M is Li and the additional dopant A is Al.

Claims 7-12 relate to a method of preparation of an oxide according to claim 1-6.

Claims 13, 14 relate to the use of the oxide of claim 1-6 in a electrochemical cell and the use of such a cell in arechargeable battery.

5. claims: 1-14 (partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Claims 1-6 relate to a lithium manganese oxide of the following composition LiMnMAO wherein M is Co and the additional dopant A is Ni.

Claims 7-12 relate to a method of preparation of an oxide according to claim 1-6.

Claims 13, 14 relate to the use of the oxide of claim 1-6 in a electrochemical cell and the use of such a cell in arechargeable battery.

6. claims: 1-14 (partially)

Claims 1-6 relate to a lithium manganese oxide of the following composition LiMnMAO wherein M is Co and the additional dopant A is Al.

Claims 7-12 relate to a method of preparation of an oxide according to claim 1-6.

Claims 13, 14 relate to the use of the oxide of claim 1-6 in a electrochemical cell and the use of such a cell in arechargeable battery.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 02/02905

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 1180810	A	20-02-2002	JP	2002063903 A		28-02-2002
			JP	2002060223 A		26-02-2002
			EP	1180810 A2		20-02-2002
			US	2002022183 A1		21-02-2002
JP 2002050401	A	15-02-2002		NONE		
US 2002012830	A1	31-01-2002	JP	2002042893 A		08-02-2002
JP 2001328818	A	27-11-2001		NONE		
EP 1130665	A	05-09-2001	JP	2001250551 A		14-09-2001
			DE	60100515 D1		04-09-2003
			DE	60100515 T2		04-03-2004
			EP	1130665 A1		05-09-2001
			US	2001024753 A1		27-09-2001
JP 2001167763	A	22-06-2001		NONE		
JP 2001143710	A	25-05-2001	KR	2001047099 A		15-06-2001
			US	6274273 B1		14-08-2001
US 6274273	B1	14-08-2001	KR	2001047099 A		15-06-2001
			JP	2001143710 A		25-05-2001
WO 0115252	A	01-03-2001	WO	0115252 A1		01-03-2001
			JP	2001126731 A		11-05-2001
			JP	2001261341 A		26-09-2001
			JP	2001261342 A		26-09-2001
JP 2001023640	A	26-01-2001		NONE		
WO 0101505	A	04-01-2001	JP	2001202962 A		27-07-2001
			WO	0101505 A1		04-01-2001
US 6168887	B1	02-01-2001		NONE		
JP 20000294242	A	20-10-2000		NONE		
JP 11339771	A	10-12-1999		NONE		
JP 11067209	A	09-03-1999		NONE		
WO 9905734	A	04-02-1999	WO	9905734 A1		04-02-1999
			US	6458487 B1		01-10-2002
US 6458487	B1	01-10-2002	WO	9905734 A1		04-02-1999
JP 08273665	A	18-10-1996	JP	3506397 B2		15-03-2004
US 6214493	B1	10-04-2001	AU	713144 B2		25-11-1999
			AU	1387597 A		11-08-1997
			CA	2242901 A1		24-07-1997
			EP	0875080 A1		04-11-1998
			WO	9726683 A1		24-07-1997
			JP	2000503453 T		21-03-2000